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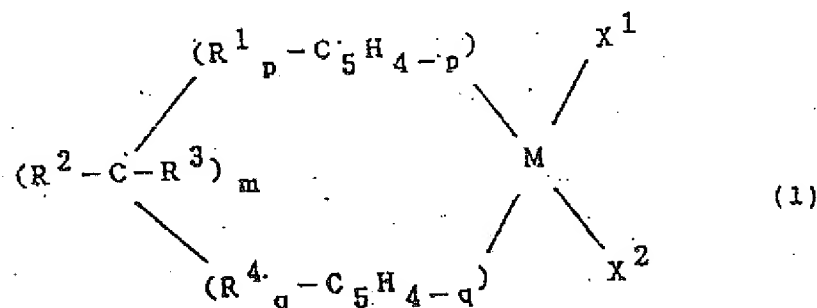
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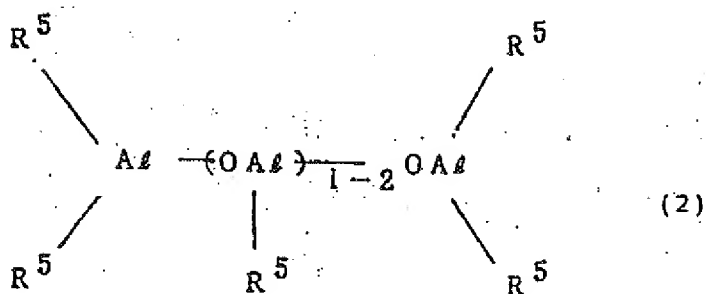
(54) Catalyst for polymerization of olefins and process for production of olefin polymers.

(57) A catalyst for the polymerization of olefins is provided which comprises a solid catalyst component (A) derived by supporting a transition metal compound represented by the general formula (1):

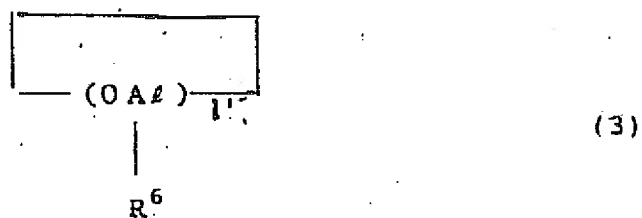


onto a solid inorganic compound, and then washing the solid inorganic compound with a nonaqueous solvent capable of dissolving the transition metal compound, wherein M is a transition metal of Group 4b; X<sup>1</sup> and X<sup>2</sup> are independently a halogen, hydrogen, an alkylalkoxy group, or a saturated or unsaturated alkyl group which groups may be linked together to form a bond; R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are independently hydrogen or a saturated or unsaturated alkyl group of 1 to 100 carbon atoms which groups may be linked together to form a bond; m is an integer of 1 to 6; and p and q are independently an integer of 0 to 4, and a catalyst component (B) comprising an organic aluminum compound represented by the general formula (2) and/or (3):

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wherein  $1$  is an integer of 2 to 100,  $R^5$  is a saturated or unsaturated alkyl group of 1 to 6 carbons,



wherein  $1'$  is an integer of 2 to 100,  $R^6$  is a saturated or unsaturated alkyl group of 1 to 6 carbons. A process for producing olefin polymers was also provided in which the aforementioned catalyst is employed. This catalyst is prepared with less amount of organic aluminosilane, yet has high activity.

The present invention relates to a catalyst which comprises a transition metal compound having a high activity for the polymerization of olefins. The present invention also relates to a process for producing olefin polymers by use of the catalyst.

As an olefin polymerization catalyst, soluble metallocene catalysts are well known which are based on a combination of a bis(cyclopentadienyl)titanium-alkyl or a bis(cyclopentadienyl)titanium halide, as a transition metal compound, with an organoaluminum compound. An example thereof is disclosed in U.S. Patent 4,522,982. In such catalysts, the organoaluminum compound is used in an amount of several thousand times the transition metal compound to obtain high catalyst activity. Aluminum compounds, however, are very expensive, so that the catalysts are not suitable for industrial production of general-purpose polyolefin resins.

An isotactic polypropylene is produced by suspension polymerization by use of a catalyst comprising an aluminum compound and ethylene-bis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride as a transition metal compound (see e.g., EP-A-185,918).

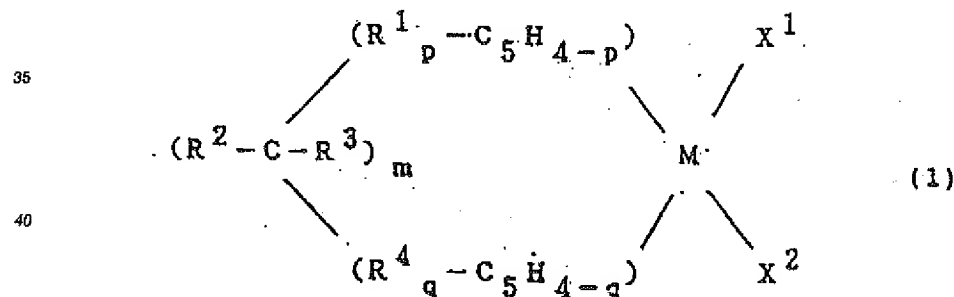
In this polymerization process also, a large amount of an organic aluminum compound is necessarily required to obtain high catalyst activity, resulting in low activity for aluminum of the organic aluminum compound.

In another process, polypropylene is produced without accumulation of the polymer onto the wall of a reaction vessel by use of a catalyst comprising a solid component derived by bringing dimethylsilyl-bis(2,4-dimethylcyclopentadienyl)zirconium dichloride as a transition metal compound into contact with an organic aluminum compound-treated silica, and methylaluminum compound as an organic aluminum compound (Japanese Patent Application Laid-open No. Hei-3-74412). In this polymerization process also, the organoaluminum compound is used in a large amount in the preliminary treatment of silica and polymerization, resulting in low activity for aluminum of the organic aluminum compound.

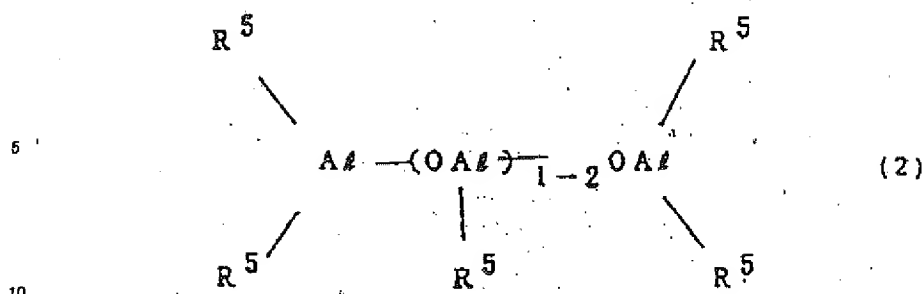
The object of the present invention is to solve the above problems of the prior art. This object has been solved by the use of a transition metal compound supported by a solid inorganic compound which enables the decrease of the amount of the expensive organic aluminum compound and yet gives a highly active catalyst for olefin polymerization.

The present invention provides a novel catalyst for the polymerization of olefins, the catalyst employing a transition metal compound and a decreased amount of the expensive organic aluminum compound, and yet having a high catalytic activity.

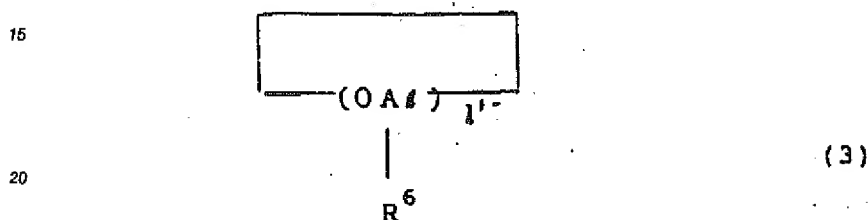
The present invention provides a catalyst for the polymerization of olefins, comprising a solid catalyst component (A) derived by depositing a transition metal compound represented by the general formula (1):



onto a solid inorganic compound, and then washing the solid inorganic compound with a nonaqueous solvent capable of dissolving the transition metal compound, wherein M is a transition metal of Group 4b; X<sup>1</sup> and X<sup>2</sup> are independently a halogen, hydrogen, an alkylalkoxy group, or a saturated or unsaturated alkyl group which groups may be linked together to form a bond; R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are independently hydrogen or a saturated or unsaturated alkyl group of 1 to 100 carbon atoms which groups may be linked together to form a bond; m is an integer of 1 to 6; and p and q are independently an integer of 0 to 4, and a catalyst component (B) comprising an organic aluminum compound represented by the general formula (2) and/or (3):



wherein 1 is an integer of 2 to 100,  $R^5$  is a saturated or unsaturated alkyl group of 1 to 6 carbons.



wherein 1' is an integer of 2 to 100,  $R^6$  is a saturated or unsaturated alkyl group of 1 to 6 carbons.

The present invention also provides a process for producing olefin polymers employing the above catalyst for the polymerisation of the olefins.

The transition metal compound in the catalyst component (A) of the olefin polymerization catalyst of the present invention is represented by the general formula (1). The transition metal M in the general formula is an element of Group 4b of Periodic Table, including titanium, zirconium, and hafnium, among which zirconium and hafnium are preferred.

$X^1$  and  $X^2$  are independently a halogen, hydrogen, an alkylalkoxy group, or a saturated or unsaturated alkyl group. The halogen includes specifically fluorine, chlorine, bromine, and iodine, among which chlorine is preferred. The alkylalkoxy group includes primary, secondary, and tertiary alkylalkoxy groups of 1 to 100 carbon atoms, preferably 1 to 6 carbon atoms. The saturated or unsaturated alkyl group includes hydrocarbon groups of 1 to 100 carbon atoms, preferably 1 to 6 carbon atoms. The saturated or unsaturated alkyl groups of 1 to 6 carbon atoms are linear, branched, or cyclic alkyl groups, specifically including methyl, ethyl, ethenyl, n-propyl, isopropyl, propenyl, n-butyl, isobutyl, t-butyl, butenyl, n-pentyl, isopentyl, t-pentyl, pentenyl, n-hexyl, isohexyl, cyclohexyl, benzyl, and the like.  $X^1$  and  $X^2$  may be the same or different, or may be linked together to form a bond. The linked alkyl group includes linear, branched, or cyclic bivalent alkyl groups such as ethylene, trimethylene, propenylene, tetramethylene, butylenylene, pentamethylene, pentenylene, hexamethylene, hexenylene, cyclohexenylene, and benzyldiene.

$R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are independently hydrogen or a saturated or unsaturated hydrocarbon group of 1 to 100 carbon atoms, preferably hydrogen or a hydrocarbon group of 1 to 6 carbon atoms. The alkyl or alkenyl group of 1 to 6 carbon atoms include linear, branched and cyclic alkyl groups such as methyl, ethyl, ethenyl, n-propyl, isopropyl, propenyl, n-butyl, isobutyl, t-butyl, butenyl, n-pentyl, isopentyl, t-pentyl, pentenyl, n-hexyl, isohexyl, cyclohexyl, and benzyl.

The groups of  $R^2$  and  $R^3$ , the two  $R^1$  groups when p is 2 or more, and the two  $R^4$  groups when q is 2 or more may respectively linked together to form a bond. The linked group includes linear, branched, or cyclic bivalent alkyl groups such as ethylene, trimethylene, propenylene, tetramethylene, butenylene, butadienylene, pentamethylene, pentenylene, hexamethylene, hexenylene, cyclohexenylene, and benzyldiene.

The size (m) of the linking group between the two cyclopentadienyl groups or derivatives thereof is denoted by an integer of 1 to 6, preferably 1 or 2. The symbols of p and q, which may be the same or different, are respectively a number of the substituents on the cyclopentadienyl ring, and are an integer of 0 to 4.

The transition metal compounds used for forming the catalyst component (A), in the case where the transition metal M is zirconium, and  $X^1$  and  $X^2$  are chlorine, includes:

- methylenebis(cyclopentadienyl)zirconium dichloride,  
 methylenebis(2-methylcyclopentadienyl)zirconium dichloride,  
 methylenebis(3-methylcyclopentadienyl)zirconium dichloride,  
 methylenebis(2-methylcyclopentadienyl)(3-methylcyclopentadienyl)zirconiumdichloride,  
 5 methylenebis(2,3-dimethylcyclopentadienyl)zirconium dichloride,  
 methylenebis(2,4-dimethylcyclopentadienyl)zirconium dichloride,  
 methylenebis(2,5-dimethylcyclopentadienyl)zirconium dichloride,  
 methylenebis(3,4-dimethylcyclopentadienyl)zirconium dichloride,  
 methylene(2,3-dimethylcyclopentadienyl)(2,4-dimethylcyclopentadienyl)zirconium dichloride,  
 10 methylene(2,3-dimethylcyclopentadienyl)(2,5-dimethylcyclopentadienyl)zirconium dichloride,  
 methylene(2,3-dimethylcyclopentadienyl)(3,4-dimethylcyclopentadienyl)zirconium dichloride,  
 methylene(2,4-dimethylcyclopentadienyl)(2,5-dimethylcyclopentadienyl)zirconium dichloride,  
 methylene(2,4-dimethylcyclopentadienyl)(3,4-dimethylcyclopentadienyl)zirconium dichloride,  
 methylenebis(2,3,4-trimethylcyclopentadienyl)zirconium dichloride,  
 15 methylenebis(2,3,5-trimethylcyclopentadienyl)zirconium dichloride,  
 methylenebis(2,3,4,5-tetramethylcyclopentadienyl)zirconium dichloride,  
 methylenebis(ethylcyclopentadienyl)zirconium dichloride,  
 methylenebis(diethylcyclopentadienyl)zirconium dichloride,  
 methylenebis(indenyl)zirconium dichloride,  
 20 isopropylidene(cyclopentadienyl-methylcyclopentadienyl)zirconium dichloride,  
 isopropylidene(cyclopentadienyl-dimethylcyclopentadienyl)zirconium dichloride,  
 isopropylidene(cyclopentadienyl-trimethylcyclopentadienyl)zirconium dichloride,  
 isopropylidene(cyclopentadienyl-tetramethylcyclopentadienyl)zirconium dichloride,  
 isopropylidene(cyclopentadienyl-ethylcyclopentadienyl)zirconium dichloride,  
 25 isopropylidene(cyclopentadienyl-diethylcyclopentadienyl)zirconium dichloride,  
 isopropylidene(cyclopentadienyl-triethylcyclopentadienyl)zirconium dichloride,  
 isopropylidene(cyclopentadienyl-tetraethylcyclopentadienyl)zirconium dichloride,  
 isopropylidene(cyclopentadienyl-fluorenyl)zirconium dichloride,  
 isopropylidene(cyclopentadienyl-2,7-di-t-butylfluorenyl)zirconium dichloride,  
 30 isopropylidene(cyclopentadienyl-octahydrofluorenyl)zirconium dichloride,  
 isopropylidene(methylcyclopentadienyl-fluorenyl)zirconium dichloride,  
 isopropylidene(dimethylcyclopentadienyl-fluorenyl)zirconium dichloride,  
 isopropylidene(trimethylcyclopentadienyl-fluorenyl)zirconium dichloride,  
 isopropylidene(tetramethylcyclopentadienyl-fluorenyl)zirconium dichloride,  
 35 isopropylidene(ethylcyclopentadienyl-fluorenyl)zirconium dichloride,  
 isopropylidene(diethylcyclopentadienyl-fluorenyl)zirconium dichloride,  
 isopropylidene(methylcyclopentadienyl-2,7-di-t-butylfluorenyl)zirconium dichloride,  
 isopropylidene(dimethylcyclopentadienyl-2,7-di-t-butylfluorenyl)zirconiumdichloride,  
 isopropylidene(trimethylcyclopentadienyl-2,7-di-t-butylfluorenyl)zirconium dichloride,  
 40 isopropylidene(tetramethylcyclopentadienyl-2,7-di-t-butylfluorenyl)zirconium dichloride,  
 isopropylidene(ethylcyclopentadienyl-2,7-di-t-butylfluorenyl)zirconium dichloride,  
 isopropylidene(diethylcyclopentadienyl-2,7-di-t-butylfluorenyl)zirconium dichloride,  
 isopropylidene(methylcyclopentadienyl-octahydrofluorenyl)zirconium dichloride,  
 isopropylidene(dimethylcyclopentadienyl-octahydrofluorenyl)zirconium dichloride,  
 45 isopropylidene(trimethylcyclopentadienyl-octahydrofluorenyl)zirconium dichloride,  
 isopropylidene(tetramethylcyclopentadienyl-octahydrofluorenyl)zirconium dichloride,  
 isopropylidene(ethylcyclopentadienyl-octahydrofluorenyl)zirconium dichloride,  
 isopropylidene(diethylcyclopentadienyl-octahydrofluorenyl)zirconium dichloride,  
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 50 cyclohexylidene(cyclopentadienyl-dimethylcyclopentadienyl)zirconium dichloride,  
 cyclohexylidene(cyclopentadienyl-trimethylcyclopentadienyl)zirconium dichloride,  
 cyclohexylidene(cyclopentadienyl-tetramethylcyclopentadienyl)zirconium dichloride,  
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 cyclohexylidene(cyclopentadienyl-diethylcyclopentadienyl)zirconium dichloride,  
 55 cyclohexylidene(cyclopentadienyl-triethylcyclopentadienyl)zirconium dichloride,  
 cyclohexylidene(cyclopentadienyl-tetraethylcyclopentadienyl)zirconium dichloride,  
 cyclohexylidene(cyclopentadienyl-fluorenyl)zirconium dichloride,  
 cyclohexylidene(cyclopentadienyl-2,7-di-t-butylfluorenyl)zirconium dichloride,

cyclohexylidene(cyclopentadienyl-octahydrofluorenyl)zirconium dichloride,  
 cyclohexylidene(methylcyclopentadienyl-fluorenyl)zirconium dichloride,  
 cyclohexylidene(dimethylcyclopentadienyl-fluorenyl)zirconium dichloride,  
 cyclohexylidene(trimethylcyclopentadienyl-fluorenyl)zirconium dichloride,  
 5 cyclohexylidene(tetramethylcyclopentadienyl-fluorenyl)zirconium dichloride,  
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 cyclohexylidene(diethylcyclopentadienyl-fluorenyl)zirconium dichloride,  
 cyclohexylidene(methylcyclopentadienyl-2,7-di-t-butylfluorenyl)zirconium dichloride,  
 cyclohexylidene(dimethylcyclopentadienyl-2,7-di-t-butylfluorenyl)zirconium dichloride,  
 10 cyclohexylidene(trimethylcyclopentadienyl-2,7-di-t-butylfluorenyl)zirconium dichloride,  
 cyclohexylidene(tetramethylcyclopentadienyl-2,7-di-t-butylfluorenyl)zirconium dichloride,  
 cyclohexylidene(ethylcyclopentadienyl-2,7-di-t-butylfluorenyl)zirconium dichloride,  
 cyclohexylidene(diethylcyclopentadienyl-2,7-di-t-butylfluorenyl)zirconiumdichloride,  
 cyclohexylidene(methylcyclopentadienyl-octahydrofluorenyl)zirconium dichloride,  
 15 cyclohexylidene(dimethylcyclopentadienyl-octahydrofluorenyl)zirconium dichloride,  
 cyclohexylidene(trimethylcyclopentadienyl-octahydrofluorenyl)zirconium dichloride,  
 cyclohexylidene(tetramethylcyclopentadienyl-octahydrofluorenyl)zirconium dichloride,  
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 diphenylmethylenecyclopentadienyl-trimethylcyclopentadienylzirconium dichloride,  
 diphenylmethylenecyclopentadienyl-tetramethylcyclopentadienylzirconium dichloride,  
 diphenylmethylenecyclopentadienyl-ethylcyclopentadienylzirconium dichloride,  
 25 diphenylmethylenecyclopentadienyl-diethylcyclopentadienylzirconium dichloride,  
 diphenylmethylenecyclopentadienyl-triethylcyclopentadienylzirconium dichloride,  
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 diphenylmethylenecyclopentadienyl-2,7-di-t-butylfluorenyl)zirconium dichloride,  
 30 diphenylmethylenecyclopentadienyl-octahydrofluorenyl)zirconium dichloride,  
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 35 diphenylmethylenethylcyclopentadienyl-fluorenyl)zirconium dichloride,  
 diphenylmethylenediethylcyclopentadienyl-fluorenyl)zirconium dichloride,  
 diphenylmethylenemethylcyclopentadienyl-2,7-di-t-butylfluorenyl)zirconium dichloride,  
 diphenylmethylenedimethylcyclopentadienyl-2,7-di-t-butylfluorenyl)zirconium dichloride,  
 diphenylmethylenetrimethylcyclopentadienyl-2,7-di-t-butylfluorenyl)zirconium dichloride,  
 40 diphenylmethylenetetramethylcyclopentadienyl-2,7-di-t-butylfluorenyl)zirconium dichloride,  
 diphenylmethylenethylcyclopentadienyl-2,7-di-t-butylfluorenyl)zirconiumdichloride,  
 diphenylmethylenediethylcyclopentadienyl-2,7-di-t-butylfluorenyl)zirconium dichloride,  
 diphenylmethylenemethylcyclopentadienyl-octahydrofluorenyl)zirconium dichloride,  
 diphenylmethylenedimethylcyclopentadienyl-octahydrofluorenyl)zirconium dichloride,  
 45 diphenylmethylenetrimethylcyclopentadienyl-octahydrofluorenyl)zirconium dichloride,  
 diphenylmethylenetetramethylcyclopentadienyl-octahydrofluorenyl)zirconium dichloride,  
 diphenylmethylenethylcyclopentadienyl-octahydrofluorenyl)zirconium dichloride,  
 diphenylmethylenediethylcyclopentadienyl-octahydrofluorenyl)zirconium dichloride,  
 ethylenebis(1-indenyl)zirconium dichloride,  
 50 ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride, and the like.

For supporting the aforementioned transition metal compounds solid inorganic compounds generally employed in industry are useful. The industrially used solid inorganic compounds include oxides of typical elements such as alumina, silica, magnesia, and calcium oxide; oxides of transition metals such as titania, zirconia, and thoria, composites of these oxides; and halides such as magnesium chloride, and aluminum chloride.

The preferred solid inorganic compounds in the present invention are those having Lewis acidity. Among them, alumina is particularly preferred. The solid inorganic compounds are preferably in a particle form in a size of from 0.01 to 200  $\mu\text{m}$ , more preferably from 0.1 to 100  $\mu\text{m}$ .

The solid inorganic compound is generally treated preliminarily by calcination. The calcination is usually conducted at a reduced pressure or in a gas stream at a temperature in the range of from 100°C to 1200°C, preferably from 200°C to 900°C. Otherwise, the solid inorganic compound may be preliminarily treated with an organic or inorganic compound which is reactive to hydroxy groups or adsorbed waters on the surface of the solid.

The transition metal compound is made to be supported by the processes below, for example, but is not limited thereto:

- (a) processes comprising steps of bringing a solution of the transition metal compound in a nonaqueous solvent into contact with the solid inorganic compound, and washing the resulting solid component with a nonaqueous solvent capable of dissolving the transition metal compound,
- (b) processes comprising steps of adding the transition metal compound dissolved in a nonaqueous solvent to a nonaqueous slurry of the solid inorganic compound, and washing the resulting solid component with a nonaqueous solvent capable of dissolving the transition metal compound,
- (c) processes comprising steps of mixing the transition metal compound with the solid inorganic compound, adding a nonaqueous solvent to the mixture, thereby bringing the transition metal compound into sufficient contact with the solid inorganic compound, and then washing the resulting solid component with a nonaqueous solvent capable of dissolving the transition metal compound, and
- (d) processes comprising steps of bringing the transition metal compound into contact with the solid inorganic compound, and washing the resulting solid component with a nonaqueous solvent capable of dissolving the transition metal compound.

The nonaqueous solvent capable of dissolving the transition metal compound includes aromatic hydrocarbons such as benzene, toluene, and xylene; and halogenated hydrocarbons such as chloroform and methylene chloride. In the above supporting processes, the important point is the washing of the resulting solid component with a nonaqueous solvent capable of dissolving the transition metal compound. In this washing operation, the transition metal compound in the solid component is presumed to interact with the solid inorganic compound, and the interaction is considered to heighten the effect of the present invention.

The supporting treatment of the transition metal compound may be practiced in the presence of an organometallic compound as a third component. The organometallic compound includes organoaluminum compounds such as trimethylaluminum, triethylaluminum, and dimethylaluminum chloride; organosilicon compounds such as trimethylsilane, and dimethyldichlorosilane; and organomagnesium compounds such as dimethylmagnesium, and methylmagnesium chloride. Among them, organoaluminum compounds are preferred. In this case the organometal is used in a mole ratio of from 0.01 to 10000, preferably from 1 to 1000 to the transition metal.

The catalyst component (B) is an organoaluminum compound represented by the general formulas (2) and/or (3). In the general formulas (2) and (3),  $R^5$  and  $R^6$  are respectively a saturated or unsaturated alkyl group of 1 to 6 carbons. The alkyl group includes linear, branched, and cyclic hydrocarbon groups such as methyl, ethyl, ethenyl, n-propyl, isopropyl, propenyl, n-butyl, isobutyl, t-butyl, butenyl, n-pentyl, isopentyl, t-pentyl, pentenyl, n-hexyl, isohexyl, cyclohexyl, benzyl, etc. Among them, methyl is preferred. The symbols of 1 and 1', are respectively an integer of from 2 to 100, preferably from 6 to 50. The organoaluminum compound may be a commercial product, or may be synthesized by any known method. For example, the organoaluminum compound may be synthesized by bringing an organoaluminum compound into contact with a hydrocarbon solvent in which a crystallization water-containing salt (e.g., aluminum sulfate hydrate and other sulfate hydrate) or a small amount of water is suspended.

The ratio of the catalyst component (B) to the transition metal compound in the catalyst component (A) is in the range of from 0.1 to 4000. Sufficient activity is obtained at the ratio of 1000 or less. At the ratio of less than 0.1, the catalyst activity tends to become lower. The catalyst components (A) and (B) may be mixed prior to feeding to the reaction system, or otherwise be fed separately to the reaction system.

The olefins which can be polymerized by the process of the present invention include  $\alpha$ -olefins such as ethylene, propylene, 1-butene, 4-methyl-1-pentene, and 1-hexene; conjugated or unconjugated dienes such as butadiene and 1,4-hexadiene; aromatic vinyls such as styrene; and cyclic olefins such as cyclobutene. A mixture of two or more of these olefins may be polymerized.

The polymerization of the present invention may be conducted through any of the processes of liquid phase polymerization, gas phase polymerization, and bulk polymerization. The solvents for the liquid phase polymerization include aliphatic hydrocarbons such as pentane, hexane, heptane, octane, nonane, and decane; alicyclic hydrocarbons such as cyclohexane; and aromatic hydrocarbons such as benzene, toluene, and xylene.

The concentration of the catalyst of the present invention in the solution is preferably in the range of  $1 \times 10^{-10}$  mol/l and more, more preferably from  $1 \times 10^{-2}$  to  $1 \times 10^{-8}$  mol/l in terms of the catalyst component (A). The polymerization temperature is not limited specially, and is normally in the range of from  $-100^{\circ}\text{C}$  to  $230^{\circ}\text{C}$ . The pressure or the olefin in the reaction is not specially limited, and usually in the range of from atmospheric pressure to  $200 \text{ kg/cm}^2\text{G}$ .

The present invention is described in more detail by reference to examples without limiting the invention in any way.

In Examples, Mw denotes a weight-average molecular weight, Mw/Mn denotes molecular weight distribution measured by GPC at  $130^{\circ}\text{C}$  by use of o-dichlorobenzene as the solvent, and Tm denotes a melting point measured by DSC.

#### Example 1

##### (Preparation of Catalyst Component (A))

In an inert gas atmosphere, 8.3 ml of ethylenebis(1-indenyl)zirconium dichloride solution (10 mmol/l) in toluene and 0.8 ml of trimethylaluminum solution (2.42 mmol/l) in toluene were added to 8.24 g of alumina having been calcined at  $300^{\circ}\text{C}$  for 4 hours. The mixture was stirred at room temperature for 10 minutes. The solid product was collected by filtration, washed with 50 ml of toluene, and was dried at a reduced pressure to obtain a solid catalyst component (A). This solid component was found to contain 0.074 % by weight of zirconium by elemental analysis.

##### (Polymerization)

Into a thoroughly dried 500-ml autoclave, 100 ml of toluene, the above catalyst component (A) in an amount of 0.005 mmol in terms of zirconium, 1.1 mmol of methylaluminoxane (MAO, made by Tosoh-Akzo K.K.), and 150 ml of propylene were charged under an inert gas atmosphere. The polymerisation was conducted at  $40^{\circ}\text{C}$  for one hours. The polymerization product was washed with methanol, and dried in vacuum. The result of the polymerization is shown in Table 1.

#### Comparative Example 1

##### (Polymerization)

Into a thoroughly dried 500-ml autoclave, 100 ml of toluene, ethylenebis(1-indenyl)zirconium dichloride solution (10 mmol/l) in toluene in an amount of 0.005 mmol in terms of zirconium, 1.1 mmol of methylaluminoxane (MAO, made by Tosoh-Akzo K.K.), and 150 ml of propylene were charged under an inert gas atmosphere. The polymerization was conducted at  $40^{\circ}\text{C}$  for one hours. The polymerization product was washed with methanol, and dried in vacuum. The result of the polymerization is shown in Table 1.

#### Comparative Example 2

##### (Polymerization)

Polymerization was conducted in the same manner as in Example 1 except that the amount of the methyl aluminoxane was changed to 5.0 mmol. The result is shown in Table 1.

#### Example 2

##### (Polymerization)

Polymerization was conducted in the same manner as in Example 1 except that the polymerization was conducted at  $80^{\circ}\text{C}$ . The result is shown in Table 1.

As described above, the present invention provides an olefin polymerization catalyst by use of a transition metal compound and a decreased amount of the expensive organic aluminoxane with high activity.

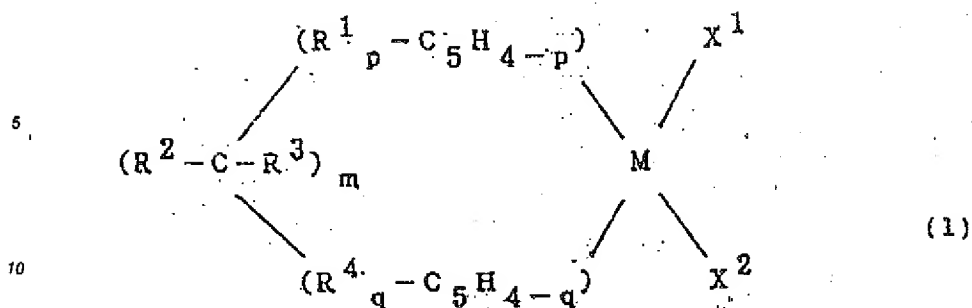


Table 1

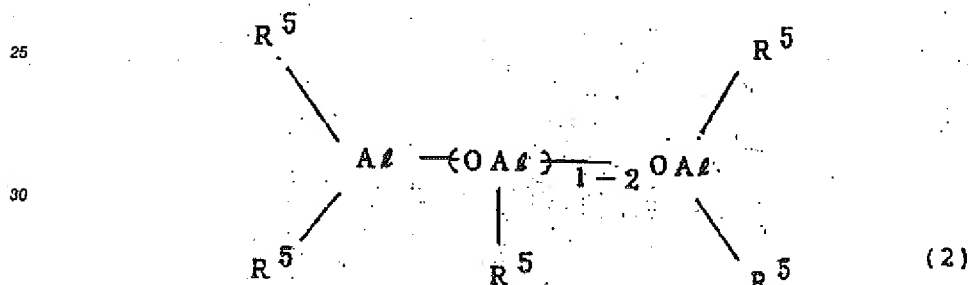
	Zirconium component (mmol)	MAO (mmol)	Yield (g)	Activity (g/mm-Al.h)	T <sub>m</sub> (°C)	M <sub>w</sub> ( $\times 10^{-4}$ )	M <sub>w</sub> /M <sub>n</sub>
Example 1	0.005	1.1	17.1	15.5	143	2.67	2.15
Comparative example 1	0.005	1.1	9.1	8.3			
Comparative example 2	0.005	5.0	40.0	8.0			
Example 2	0.005	1.1	66.0	60.0			

## Claims

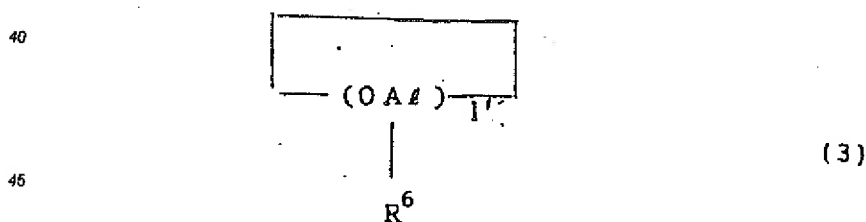
1. A catalyst for the polymerization of olefins, comprising a solid catalyst component (A) derived by supporting a transition metal compound represented by the general formula (1):



onto a solid inorganic compound, and then washing the solid inorganic compound with a nonaqueous solvent capable of dissolving the transition metal compound, wherein M is a transition metal of Group 4b; X<sup>1</sup> and X<sup>2</sup> are independently a halogen, hydrogen, an alkylalkoxy group, or a saturated or unsaturated alkyl group which groups may be linked together to form a bond; R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are independently hydrogen or a saturated or unsaturated alkyl group of 1 to 100 carbon atoms which groups may be linked together to form a bond; m is an integer of 1 to 6; and p and q are independently an integer of 0 to 4, and a catalyst component (B) comprising an organic aluminum compound represented by the general formula (2) and/or (3):

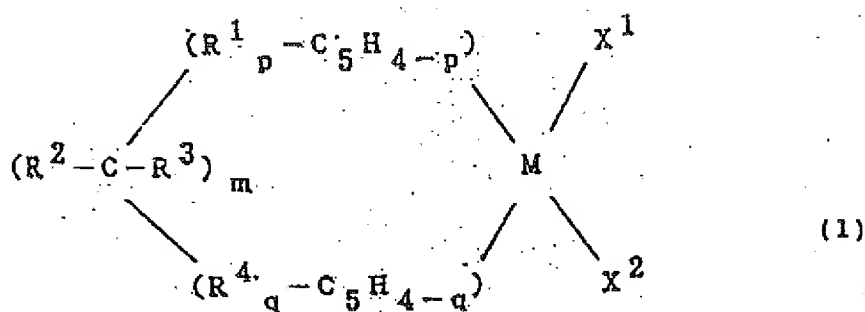


wherein 1 is an integer of 2 to 100, R<sup>5</sup> is a saturated or unsaturated alkyl group of 1 to 6 carbons,

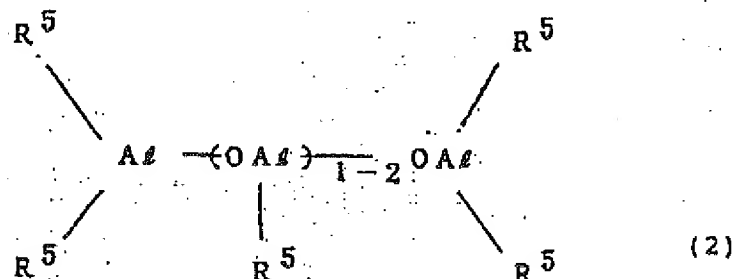


wherein 1' is an integer of 2 to 100, R<sup>6</sup> is a saturated or unsaturated alkyl group of 1 to 6 carbons.

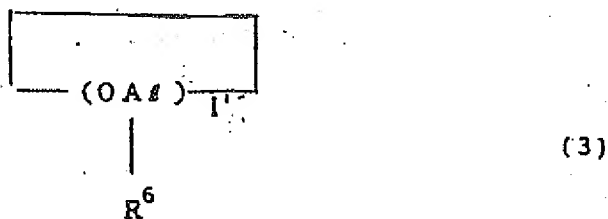
2. A process for the preparation of a catalyst for the polymerization of olefins, comprising forming a solid catalyst component (A) by supporting a transition metal compound represented by the general formula (1):



onto a solid inorganic compound, and then washing the solid inorganic compound with a nonaqueous solvent capable of dissolving the transition metal compound, wherein M is a transition metal of Group 4b; X<sup>1</sup> and X<sup>2</sup> are independently a halogen, hydrogen, an alkylalkoxy group, or a saturated or unsaturated alkyl group which groups may be linked together to form a bond; R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are independently hydrogen or a saturated or unsaturated alkyl group of 1 to 100 carbon atoms which groups may be linked together to form a bond; m is an integer of 1 to 6; and p and q are independently an integer of 0 to 4, and mixing component A with a catalyst component (B) comprising an organic aluminium compound represented by the general formula (2) and/or (3):



wherein 1 is an integer of 2 to 100, R<sup>5</sup> is a saturated or unsaturated alkyl group of 1 to 6 carbons,



where 1' is an integer of 2 to 100, R<sup>6</sup> is a saturated or unsaturated alkyl group of 1 to 6 carbons.

3. A process for producing an olefin polymer employing the catalyst of claim 1.



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number

EP 92 12 2061

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	JOURNAL OF POLYMER SCIENCE PART A: POLYMER CHEMISTRY EDITION, vol. 29, no. 11, October 1991, pages 1603-1607, New York, US; J.C.W. CHIEN et al.: "Olefin copolymerization with metallocene catalysts III. Supported metallocene/methylaluminoxane catalyst for olefin copolymerization" * Whole document *	1-3	C 08 F 4/642 C 08 F 10/00
X	DIE MAKROMOLEKULARE CHEMIE, RAPID COMMUNICATIONS, vol. 12, no. 6, June 1991, pages 367-372, Basel, CH; M. KAMINAKA et al.: "Polymerization of propene with the catalyst systems composed of Al2O3- or MgCl2-supported Et(IndH4)2ZrCl2 and AlR3 (R = CH3, C2H5)" * Whole document *	1	
E,X	EP-A-0 523 416 (HOECHST) * Claims; page 4, lines 32-35 *	1-3	TECHNICAL FIELDS SEARCHED (Int. Cl.5)  C 08 F
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 25-03-1993	Examiner DE ROECK R G O
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document  T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons * : member of the same patent family, corresponding document			